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稀土掺杂

碱土金属化合物发光材料的研制

Development of Rare-Earth doped

Alkaline-Earth Compound Luminescent Materials

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摘 要

本论文主要采用固相法制备稀土 Eu 离子掺杂的碱土硫化物、碱土钼酸盐红色荧光粉和碱土铝酸盐绿色荧光粉，系统探讨稀土离子掺杂浓度、助熔剂和碱土离子取代量对荧光粉性能的影响，还对液相法制备碱土铝酸盐荧光粉进行尝试，最后从晶体结构、能带理论、荧光光谱的角度对以上三类稀土掺杂碱土化合物发光材料的发光机理进行初步探讨。

采用固相法在还原气氛中合成以碱土硫化物为基质的用于GaN基LED的红色荧光粉 $MS:Eu^{2+}$（M 为碱土金属离子）；比较 C 粉和 N_2-H_2（V_{N2}:V_{H2}=95%:5%）还原气氛对荧光粉发光性能的影响；改变激活剂的浓度、助熔剂的种类及添加量，制备出高亮度红色荧光粉；在 $CaS:Eu^{2+}$中引入辅助激活剂 Er^{3+}、原料中添加适量助熔剂 NH_4F、基质中适当引入 Mg^{2+}可使其发光强度增强；Sr^{2+}取代 Ca^{2+}的 $Ca_{1-x}Sr_xS:Eu^{2+},Er^{3+}$荧光粉的激发峰蓝移，更好地与 GaN 基 LED 发出的 470nm 蓝光相匹配。

由于硫化物的抗氧化性和抗湿性较差，严重制约了硫化物的应用。本论文以红色荧光粉 $CaS:Eu^{2+}$为代表，采用在荧光粉表面包覆适量硅树脂膜的方法，提高其化学稳定性。通过 XRD、EDX、SEM 等方法验证硅树脂膜的存在。发光性能测试表明经过硅树脂包覆后的荧光粉的化学稳定性有较大提高。

采用高温固相法在空气中合成碱土钼酸盐为基质的红色荧光粉 $CaMoO_4:Eu^{3+}$，得到的荧光粉荧光强度较强，可见光区的激发与发射峰较尖锐，紫外区域的较宽广。在基质中用适量 W^{6+}取代 Mo^{6+}，用紫外波段激发，可实现荧光粉发射峰在 597~545nm 范围内可调，拓展其在白光 LED 领域的应用。

采用高温固相法和共沉淀法在还原气氛中合成碱土铝酸盐为基质的绿色荧光粉 $xSrO·yAl_2O_3:Eu^{2+}$，实验中通过调节碱土锶离子与铝离子的配比、稀土离子掺杂量以及不同的热处理工艺得到荧光强度较强的荧光粉。在 $4SrO·7Al_2O_3:Eu^{2+}$基质中，Ba^{2+}置换 Sr^{2+}可实现荧光粉发射峰从 488nm 蓝移至 435nm。利用共沉淀法制备$(Ba_{0.40}Sr_{0.57})O·7/4Al_2O_3:Eu_{0.03}$碱土铝酸盐荧光

粉，添加适量 H_3BO_3 作为助熔剂，发现晶粒生长层状排列明显，其荧光强度比固相法要强，尤其通过快速升温进行热处理后的样品荧光强度较强。

针对以上三类碱土金属化合物发光材料从晶体结构、能带理论、荧光光谱对其发光机理进行一定程度的探讨。

关键词：荧光粉；发光特性；碱土金属

Abstract

In this thesis, three kinds of phosphors, including rare earth ion Eu^{3+} doped alkaline-earth sulfides and alkaline-earth molybdates red emitting phosphors and alkaline-earth aluminates green emitting phosphors, were synthesized via solid-state reaction method. Meanwhile, the co-precipitation method was also applied in the synthesis of alkaline-earth aluminates. The effect of Eu^{3+} concentration, fluxes and alkaline-earth ions substitution were systematically discussed.

A kind of sulfide, $CaS:Eu^{2+}$, activated by europium ion for white LED lighting, was synthesized via solid-state reaction route under reducing atmospheres. During this processing, optimal synthesis procedure was obtained by controlling a set of parameters. Different kinds of reducing atmospheres, CO root in carbon and nitrogen-hydrogen (V_{N2}:V_{H2}=95%:5%), were compared. Brightness of $CaS:Eu^{2+}$ could be improved by the addition of flux NH_4F in addition to dopant of Er^{3+}. By changing the host of $CaS:Eu^{2+},Er^{3+}$ into $Ca_{1-x}Sr_xS:Eu^{2+},Er^{3+}$, the emission wavelengthes of phosphors could be shifted to shorter wavelengthes, which could matched with GaN-based LED better.

A novel technique to improve the stability of sulfide phosphors was developed. The red phosphors of $CaS:Eu^{2+}$ were coated with silicone resin, which were characterized by XRD, SEM and EDX. The resistance of coated phosphors against moisture was obviously enhanced without obvious loss of luminescent intensities.

Rare earth ion Eu^{3+} doped alkaline-earth molybdates phosphors, $Ca_{0.85}MoO_4:Eu_{0.15}$, were synthesized via solid-state reaction in air, and their red emitting luminescent properties were characterized. The phosphors could be effectively excited by both UV light (250~300nm) and blue light (464nm). By substitution partially of Mo^{6+} with W^{6+} for the host $Ca_{0.85}(W_xMo_{1-x})O_4:Eu_{0.15}$ ($0<x<1$), the emission wavelengthes of the samples could be shifted from 597nm to 545nm when excitated by UV light, which were suitble for the

application of white LED.

The solid-state reaction method in reducing atmospheres was also applied to obtain europium doped alkaline-earth aluminates phosphors for green emitting. The luminescent intensity of phosphors could be improved by changing the ratio x/y in the host of $xSrO{\cdot}yAl_2O_3:Eu^{2+}$, or the concentration of Eu^{2+} doping. The emission wavelengthes of the samples could be adjusted between 488nm and 435nm by changing the value x of $(Ba_xSr_{0.97-x})O{\cdot}7/4Al_2O_3:Eu_{0.03}$. The phosphors of $(Ba_{0.40}Sr_{0.57})O{\cdot}7/4Al_2O_3:Eu_{0.03}$ were also synthesized via co-precipitation route and then coated under reducing atmospheres. The luminescent intensity of the samples was higher than that synthesized by the solid state method, especially, through fast heating rate during heat treatment processes.

Key Words: Phosphor; Luminescent; Alkaline-Earth.

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